

## Complex formation, chemical exchange, species structure, and stereoselective effects in the copper(II)-L/DL-histidine systems

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### Abstract

The formation of copper(ii) complexes with L- and DL-histidine (HisH) has been studied by means of pH-potentiometry and spectrophotometry over a wide range of pH (2-14), ligand-to-metal ratio (1:1-15:1), and temperature (15-55°C) in aqueous solutions with 1.0 mol dm<sup>-3</sup> KNO<sub>3</sub> as background. Formation constants and spectral characteristics of 13 complex types were found. Fine stereoselective effects have been detected with preferential coordination of two ligands with identical configuration in Cu(His)(HisH) + and opposite configuration in Cu(His)<sub>2</sub>. The stereoselective effect for Cu(His)(HisH) + is explained by hydrogen bond formation between the carboxyl and imidazolyl groups of neighboring ligands at cis-arrangement of amino groups (3N eq-form). The opposite sign of stereoselective effect for Cu(His)<sub>2</sub> is derived from favourable axial coordination of the imidazole group in meso-form with cis-structure (3N eqN ax-form). A significant tetrahedral distortion was revealed for the first time in the prevalent cis-isomer of the Cu(L-His)<sub>2</sub> 4N eq-form. These findings were confirmed by EPR data and DFT computations at the B3LYP/TZVP level. The prevalence of cis-isomers for these complexes has been assigned to the rather strong trans effect of the amino groups. The structures of other detected complexes are briefly discussed on the basis of spectroscopic data. Chemical exchange reactions in the copper(ii)- L/dl-histidine systems have been investigated by the NMR relaxation of water protons. A unique proton exchange reaction with short-term proton dissociation from the coordinated imidazolyl group catalyzed by hydroxide ion was characterised for the first time. The discovered enantioselective effects in the ligand exchange reactions between Cu(His)<sub>2</sub> and HisH or His<sup>-</sup> species were attributed to the associative substitution mechanism. © 2012 The Royal Society of Chemistry.

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